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# **Fabrication, Characterization and Application of High Temperature Superconducting Mercury-Based Cuprate Thin Films**

AFOSR Grant/Contract #F49620-96-1-0358

Total project cost: \$325k, with a half from the state of Kansas matching

Final Report

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## **OBJECTIVES**

- \* Fabrication of Epitaxial Hg-based HTS thin films
- \* Characterization of physical properties of the film
- \* Application in microelectronics

## **STATUS OF EFFORT**

During the three-year project period, significant progress has been made by the University of Kansas group in development of novel processes for fabrication of highly volatile Hg-HTS thin films. With successes of these techniques, high-quality epitaxial Hg-HTS thin and thick films can be fabricated, for the first time since the Hg-HTSs were discovered in 1993, with high reproducibility. This triggered an extensive study of physical properties of Hg-HTS thin films, between the university of Kansas group and many other institutions in the world, based on interests in investigation of fundamental issues as well as applications in numerous devices. Such an effort has led to a much-improved understanding of the Hg-HTSs and prototypes of Hg-HTS devices have been demonstrated to have superior performance as expected. All research objectives planned for this project have been met with one exception that 2-inch Hg-HTS wafers have not been obtained so far. Although a simple explanation for this is the level of difficulties in epitaxy of Hg-HTS films was much under estimated earlier, plans to reach this goal have been formed and will be detailed later in this report.

The major experimental achievements obtained during the project period are summarized in the following session. Existing problems and possible solutions are also discussed. Details associated to each specific subject can be found in 5 US patent disclosures (2 awarded, 1 transferred to industry, and 2 pending) and 37 papers (31 published/accepted and 6 submitted) and among them, 35 are referred journal articles and 2 are conference proceedings).

## ACCOMPLISHMENTS/NEW FINDINGS

### 1. Backgrounds

The newly discovered Hg-based high-temperature superconductors (Hg-HTSs:  $\text{HgBa}_2\text{Ca}_n\text{Cu}_n\text{O}_{2n+2}$ ,  $n=1,2,3,\dots$ ) have generated much excitement due to their highest superconducting transition temperatures ( $T_c$ ) [1-5]. The ambient  $T_c$  of 135 K in  $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$  (Hg-1223) is over 40 K higher than that of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO). Under a hydrostatic pressure of 25-30 GPa, the  $T_c$ 's of Hg-1223 is above 160 K [6]. In addition, a high critical current density ( $J_c$ ) on Hg-1223 and  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$  (Hg-1212, with ambient  $T_c$  of 125 K) is suggested by the measurement of the irreversibility line [7,8]. Since higher  $T_c$  and  $J_c$  imply higher operation temperatures and better performance and reliability at a given temperature, as shown recently [9-12], Hg-HTSs are very promising for applications in electronic as well as electrical devices including superconducting quantum interference devices, microwave components/systems, superconducting power transmission cables, high-field magnets, etc.

Similar to other high temperature superconductors, Hg-HTSs have layered structures. The physical properties of Hg-HTSs are highly anisotropic along the directions parallel (ab-plane) and perpendicular to (c-axis) the layers. In order to optimize device performance, large-scale epitaxy of Hg-HTSs is indispensable to both the thin-film-based electronic applications or the thick-film-based electric applications. The highly volatile and toxic nature of the Hg-based compounds, however, makes epitaxy of Hg-HTSs the toughest challenge so far in the field of HTS thin films. In contrast to an extensive effort worldwide, progress achieved in epitaxial growth of Hg-HTS thin and thick films is unsatisfactory, which significantly hindered applications of these materials in the past.

Several groups have reported fabrication of c-axis-oriented Hg-1212 [13-19] and Hg-1223 films [18-24] using a conventional thermal-reaction process. In such a process, Hg-HTSs are formed from a mixture of oxides of Ba, Ca, and Cu (Ba-Ca-Cu-O precursor) reacted at high temperatures (typically in the range of 750-860 °C) in controlled Hg-vapor pressures of ~3-10 atmospheres. Since Hg-HTSs are formed through solid/vapor reaction during the Hg-vapor annealing, processing parameters, such as Hg-vapor partial pressure ( $P_{\text{Hg}}$ ) and annealing temperature ( $T_{\text{Hg}}$ ), need to be controlled precisely in order to maintain the required phase equilibrium for Hg-HTSs [25]. In order to achieve the phase equilibrium, Wang *et al* [13] first used two pellets: one with nominal composition of  $\text{Ba}_2\text{CaCu}_2\text{O}_x$  and the other  $\text{HgBa}_2\text{CaCu}_2\text{O}_x$ . The two pellets and the Ba-Ca-Cu-O precursor films were encapsulated in a quartz ampoule to control the  $P_{\text{Hg}}$  for growth of Hg-1212 films. The phase equilibrium may be varied by choosing appropriate ratio between the weight of the  $\text{HgBa}_2\text{CaCu}_2\text{O}_x$  pellet and the volume of the quartz ampoule. Although their films had a diamagnetic transition at around 120 K, the resistive transition is incomplete due to dominance of impurity phase induced possibly by air detrimental effect on the precursor film. Tsuei *et al* [14] used more delicate precursor films, the atomic-scale mixture of HgO and Ba-Ca-Cu-O precursor made by layer-by-layer pulsed laser deposition. Hg-1212 films of  $T_c \sim 124$  K were obtained on  $\text{SrTiO}_3$  substrates with relatively good  $J_c$ s [26]. Application of the same method to Hg-1223 films, however, resulted in low phase purity (<

30%) and degraded superconducting properties. Two problems were identified: large amount of impurity phases formed during a long period of sample heating (typically a few hours) and severe film/substrate reaction. The former is caused by premature reaction of Hg vapor with Ca- and Ba-oxides in the precursor film starting at above 500 °C and the latter, by Hg-activated chemical diffusion across the film/substrate which worsens with increasing Hg-vapor annealing period.

Despite the high  $T_c$ s reported by many groups, the  $J_c$ s of these Hg-HTS films were significantly lower than that expected from the study of irreversibility line [7,8] due to the low-phase purity and poor-quality epitaxy of these films. The microwave surface resistance ( $R_s$ ) of these Hg-HTS films is an order of magnitude higher [27] than that of YBCO at 77 K and 10 GHz. The difficulties in epitaxy of high-purity Hg-HTS films are three folds in the conventional thermal-reaction process. First, it is nearly impossible to precisely control the processing parameters, such as  $P_{Hg}$ , due to the highly volatile nature of the Hg-based compounds. This makes it difficult to achieve the required phase equilibrium and results in typically multiple superconducting phases plus significant amount of non-superconducting impurities in Hg-HTS samples. Moreover, such a stringent requirement of phase equilibrium makes it nearly impossible to scale up the conventional thermal-reaction process for large-area Hg-HTS film epitaxy. All Hg-HTS films reported so far only have a dimension of a few millimeters, in contrast to that of 2 inch or larger necessary for applications. Second, that Hg-vapor reacts with most metals and oxides prohibits epitaxial growth of Hg-HTS thin films on most technologically compatible substrates. Even on few chemically stable substrates such as  $SrTiO_3$ , serious chemical diffusion on the film/substrate interface was observed [15]. Consequently, most Hg-HTS films have to be made with large thickness  $\sim 1\mu m$  and most of them are c-axis-oriented uni-axial films with rough surface morphology [28]. This explains the observed low  $J_c$ s and high  $R_s$ s on Hg-HTS films. Finally, the Ba-Ca-Cu-O precursor films are extremely sensitive to the air. As short as few-second air exposure may result in samples with severely degraded superconducting properties. Even with special sample handling, such as use of dry boxes, sample reproducibility is poor. Improvement of sample reproducibility were reported by several groups using chemical-doping-assisted growth, including Re- [17,23,24], Tl- [29], Hg- [14,17], Pb- [16], alkali (Li and Na)-doping [30,31] in the Ba-Ca-Cu-O precursor films, or by partial substitution of HgO with Hg-halides [32] or  $Tl_2O_3$  [22] in the Hg-source pellet. Nevertheless, epitaxy of Hg-HTS films remains to be a tough challenge.

## **2. Development of Novel Processes for Epitaxy of Hg-HTS Thin Films**

### **2.1 Growth Mechanism of Hg-HTS Thin Films in a Fast Temperature Ramping Annealing Process (FTRA)**

To reduce the unnecessary high-temperature processing period, we developed a fast temperature ramping Hg-vapor annealing (FTRA) process [18-21]. The quality and sample reproducibility are considerably improved on FTRA processed Hg-1212 and Hg-1223 films. The Hg-1223 films made in FTRA process has phase purity up to 80% and  $T_c > 130K$  and partial epitaxy was obtained in Hg-1212 films grown on  $SrTiO_3$  substrates [15]. FTRA process consists

of two steps: deposition of precursor Ba-Ca-Cu-O films and followed by annealing of these films in controlled Hg-vapor pressure in a sealed quartz tube. The FTRA process employs fast heating from room temperature to  $T_{Hg}$  (~780-860 °C), typically in 5-20 minutes which is an order of magnitude shorter than that used previously. This benefits film growth by suppressing the premature reaction of Hg with Ca or Ba and by reducing the unnecessary film/substrate interface chemical diffusion, which have been the main difficulties in fabrication of Hg-HTS thin films caused by the high volatility of Hg-based compounds. Consequently, the quality of the film including the phase purity, crystalline structure, surface and film/substrate interface morphology, have been substantially improved.

We have systematically studied the effects of precursor-film composition and post Hg-vapor-annealing conditions on the physical properties of Hg-1212 and Hg-1223 thin films. It has been found that the stoichiometric precursor composition is necessary to obtain good-quality films but may still result in poor-quality films if the precursor is exposed to air. Two methods were employed to solve this problem: dry-box sample preparation to minimize air exposure or doping Tl in Ba-Ca-Cu-O films to prevent air contamination of precursor films. On the other hand, processing parameters in Hg-vapor annealing, such as  $T_{Hg}$ ,  $P_{Hg}$ , heating and cooling rates, annealing period, and post-oxygen-annealing conditions, were studied in correlation with film quality. Optimized processing windows have been obtained for both c-axis-oriented Hg-1212 and Hg-1223 films. Although details may be found from the publications listed in the following, several general rules can be summarized. (1) Fast heating is favorable to prevent premature reaction of Hg with Ca or Ba and to reduce the unnecessary film/substrate interface chemical diffusion; (2) Slow cooling facilitates in-plane alignment of Hg-HTS grains and surface morphology of the film; (3) A dynamic phase equilibrium is the key to the success of the FTRA process since sample heating is fast and Hg-based compound is too volatile. This equilibrium can be achieved by placing the precursor film in close proximity (< 0.3 mm) of the Hg-Ba-Ca-Cu-O source. A special sample configuration was developed (patent pending) and good sample reproducibility has been obtained. Table 1 summarizes some physical properties of Hg-1212 and Hg-1223 films obtained in FTRA process.

Table 1. Superconducting properties of Hg-HTS films made in FTRA process

	substrate	$T_c(K)$	$J_c(5K,0T)$ $10^6 A/cm^2$	$J_c(5K,5T)$ $10^6 A/cm^2$	$J_c(77K,0T)$ $10^6 A/cm^2$	$J_c(100K,0T)$ $10^6 A/cm^2$	$J_c(110K,0T)$ $10^6 A/cm^2$
Hg-1212	SrTiO <sub>3</sub> , LaAlO <sub>3</sub>	120-124	15-20	1.5-2	1.4-2.1	0.1-0.3	0.05-0.1
Hg-1223	SrTiO <sub>3</sub> , LaAlO <sub>3</sub>	127-130	18-21	2-3	2.2-2.5	0.2-0.5	0.1-0.2

## 2.2 Chemical-Doping-Assisted Growth of Hg-HTSs

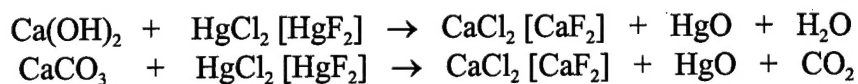
The motivation for chemical-doping-assisted growth was two-folded: to ease the film fabrication process and to improve the physical properties of the film. Three groups of doping



were studied systematically including alkali doping (Li, Na and K, doped directly in precursor films), halogen doping (F and Cl, doped in the Hg source) and heavy metals (Tl, Pb, and Re, doped in either precursors or the Hg source).

**Alkali doping** in Hg-1223 films and bulks has been found beneficial in four aspects: increasing the onset  $T_c$  to above 140 K, increasing the irreversibility line, promoting Hg-1223 phase formation, and decreasing the annealing temperature by over 100 °C which is promising for the growth of Hg-1223 thin films on many technologically compatible substrates. The mechanism of the alkali doping is still under investigation. High-resolution transmission electron microscopy (HRTEM) suggested that it is unlikely for alkali to enter the lattice. Evidence of promoted grain growth and connection in doped samples indicates alkali serves as flux, which catalyzes growth of Hg-HTS phase. The alkali may remain as interstitials, which perturbs the local distribution of oxygen in the Hg-O plane as suggested by an unusual temperature-dependence of resistivity in normal state.

**Halogen doping** ( $\text{HgCl}_2$  or  $\text{HgF}_2$ ) was found to be an effective way to decompose the contaminated precursors (containing Ca- or Ba-carbonates/hydroxides) when added as a part of the Hg-source via possibly the following reactions:



The  $\text{CaCl}_2$  or  $\text{BaCl}_2$  ( $\text{CaF}_2$  or  $\text{BaF}_2$ ) behaves as a Ca- (or Ba-) source which decomposes at  $T_{\text{Hg}}$ . Adding a small amount of  $\text{HgCl}_2$  or  $\text{HgF}_2$  (to replace 10-20% of  $\text{HgO}$  per formula), therefore, could prevent off-stoichiometry in the contaminated precursor film. Consequently, the phase purity of Hg-HTS films grown with assistance of halogen doping was improved to above 90%.

**Tl (Pb and Re) doping** (up to 20% per formula) in the precursor films has also been investigated on Hg-1223 and Hg-1212 films while the effect of doping is not significant. For Tl-doping, although  $T_c$  in the doped bulk can be raised to 138-141 K, the  $T_c$  in the doped Hg-1223 films is only up to 131 K, which is comparable with that for undoped Hg-1223 thin films. For Pb-doping, the superconducting grains seem to have larger sizes and can be formed at slightly lower annealing temperatures. Even with Re-doping, the sample quality does not seem to be much different from that of the undoped samples. Typically,  $J_c$ s in the doped films are comparable or lower than that of undoped films.

### 2.3 Invention of a Hg-Tl Cation-Exchange Process

We have also explored new processes for high-quality epitaxy of Hg-HTS thin films and found that **Tl-Hg cation exchange** can be applied as a new scheme for epitaxial growth of Hg-HTS thin films (patent pending). In the cation-exchange process, superconducting  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$  (Tl-1212) and  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  (Tl-2212) thin films were employed to form Hg-1212 and  $\text{TlBa}_2\text{Ca}_2\text{Cu}_2\text{O}_9$  (Tl-1223), and  $\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  (Tl-2223) to form Hg-1223 films, via Tl-Hg

cation exchange. This process eliminates the stringent requirements of phase diagram in the conventional process and results in a significantly improved sample quality and reproducibility.

A recently developed cation-exchange process (developed in this project period by our group) offers a promise to circumvent major problems in epitaxy of Hg-HTS films [33]. This process is composed of two steps: selection of a precursor matrix is followed by cation exchange. In Fig. 1, a comparison of the conventional thermal process (Fig. 1A) and the cation-exchange process (Fig. 1B) is schematically described. In the cation-exchange process, the precursor matrices are chosen to have a similar structure and composition to that of the target material and to have at least one weakly bonded cation (cation "b") to be replaced by the desired cation (cation "a") to form the target material. When the cation "b" is perturbed using various different methods such as thermal heating or light/particle-beam irradiation, it will vibrate around the equilibrium site where the Gibbs free energy is minimized. The spatial deflection of this cation is proportional to the energy of perturbation. When the threshold perturbation energy ( $U_{th}$ ) is reached, at which the deflection of cation "b" is comparable to the lattice constant, the precursor matrix may collapse due to quick escape of many cation "b". In the cation-exchange process, however, the perturbation energy is maintained to be close to but below  $U_{th}$  so that the precursor matrix is well kept while the cation "b" is slowly escaping. If a vapor of cation "a" is provided simultaneously, the overwhelming population of cation "a" may induce the replacement of cation "b" with cation "a" and the target material is formed.

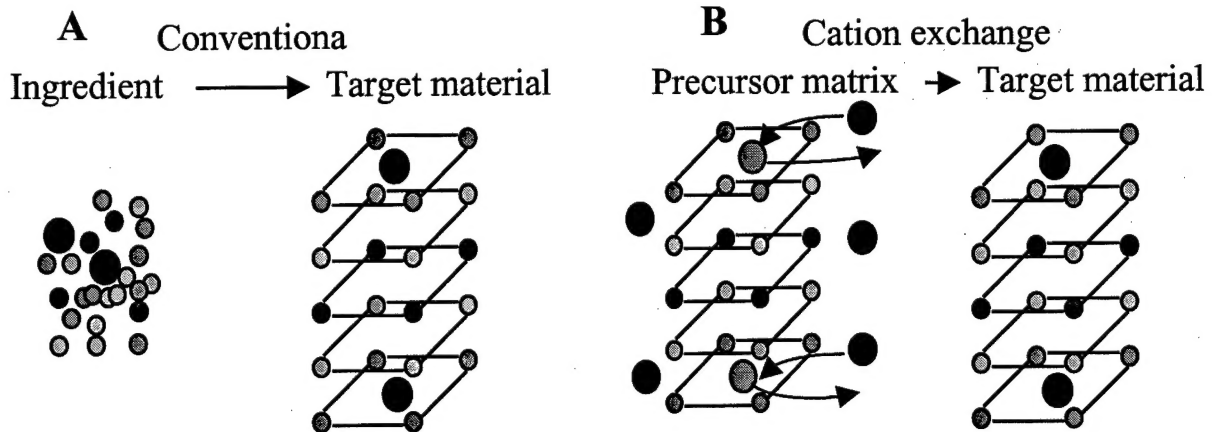


Fig. 1. Schematic description of the conventional (panel A) and the cation-exchange (panel B) processes.

The cation-exchange process employs a completely different growth mechanism. It does not require phase equilibrium and allows epitaxy of Hg-HTSs through a kinetic diffusion so that it can be carried out effectively in a large processing window [33]. Fig. 2 includes preliminary data on Hg-1212 films formed via Hg-Tl cation exchange from  $Tl_yBa_2Ca_{n-1}Cu_nO_x$  (Tl-HTSs:  $y=1,2$  and  $n=2$  or  $3$ ) precursor matrices. Fig. 2A shows that three Hg-1212 films processed at dramatically different  $P_{Hg}$  of  $1 P_0$ ,  $0.75 P_0$  and  $0.5 P_0$  have nearly identical  $T_c$ s and  $J_c$ s. Fig. 2B depicts results for two Hg-1212 films with one annealed at  $700^\circ C$  for 12 hours and the other at  $780^\circ C$  for 3 hours in the cation-exchange process. Again, both  $T_c$ s and  $J_c$ s are nearly the same in these films while the processing conditions are far from the required phase equilibrium,  $P_{Hg} \approx 1 P_0$ .

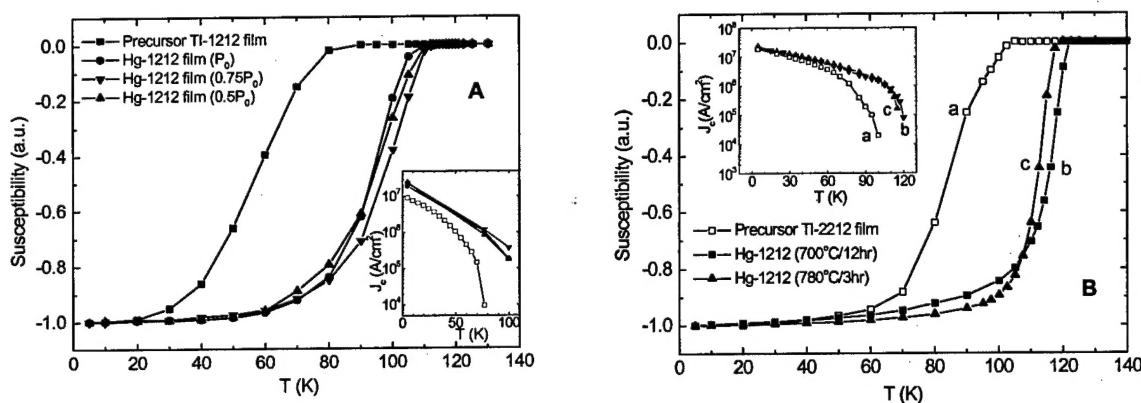


Fig. 2. Magnetic susceptibility vs. temperature curves for Hg-1212 thin films processed via Hg-Tl cation exchange at different  $P_{Hg}$  of 1  $P_0$ , 0.75  $P_0$  and 0.5  $P_0$  but same  $T_{Hg} = 750$  °C for  $t_{Hg}$  of 3 hours from Tl-1212 precursor matrices (Panel A); and at different  $T_{Hg}$  and  $t_{Hg}$  of 700 °C for 12 hours or 780 °C for 3 hours (Panel B) from Hg-2212 precursor matrices.  $P_0$  represents the equilibrium  $P_{Hg}$  at  $\sim 750$  °C. The insets show comparisons of  $J_c$ s of these Hg-1212 films.

and  $T_{Hg} \sim 800$  °C, for Hg-1212. Hg-1212 and Hg-1223 thin films processed via cation exchange inherit high-quality epitaxy and smooth surface morphology from their precursor matrices [34,35]. Consequently, the quality of the film made in cation-exchange process is superior to that made in the conventional process. For example, their  $J_c$ s close to 1 MA/cm<sup>2</sup> at 110K, as shown in Fig. 2B, are nearly an order of magnitude higher than the best value reported previously on Hg-HTS thin film [26,20,21] and can be further improved with optimization of processing conditions.  $R_s$  of  $\sim 0.6$  m $\Omega$  at 100 K and 10 GHz obtained recently on the Hg-1212 films [27] is comparable to that of YBCO films at 77 K and several orders of magnitude smaller than that on Hg-HTS films made in conventional process.

**Table 2. Current Status of Hg-HTS films  
(by the cation-exchange process)**

<b>Phase Purity:</b>	<b>&gt; 95%</b>
$\chi_{min}$ (RBS/chann):	<b><math>\sim 12\%</math></b>
<b>Area:</b>	<b>20x20 mm<sup>2</sup></b>
<b>Thickness:</b>	<b>0.05-1 <math>\mu</math>m</b>
<b><math>T_c</math>:</b>	<b>120-130K</b>
<b><math>J_c</math> at 100K:</b>	<b>1.5-2MA/cm<sup>2</sup></b>
<b><math>J_c</math> at 110K:</b>	<b>0.5-1MA/cm<sup>2</sup></b>
<b><math>R_s</math>(120K,10GHz):</b>	<b><math>\sim 0.3</math> m<math>\Omega</math></b>
<b>Loss(115K,10GHz):</b>	<b>&lt;0.5 dB</b>



## Related Publications

1. U.S. patent #5883050 (1999), by S.H. Yun and J.Z. Wu, "Hg-Based Superconducting Cuprate Films and Methods and Apparatus for Preparing the Same".
2. Y.Y. Xie, J.Z. Wu, S.L. Yan, Y. Yu, T. Aytug and L. Fang, "Elimination of Air Detrimental Effect using Tl-assisted Growth process for Hg-1212 Thin Films", submitted to Physica C.
3. J.Z. Wu, D. Eckart, S. H. Yun, and S. Tidrow, "Microstructures of Hg-Based Cuprate Thin Films", Physica C, **271**, 1(1996).
4. J.Z. Wu, S.H. Yun, A. Gapud, B.W. Kang, W.N. Kang, S.C. Tidrow, T.P. Monahan, X.T. Cui and W.K. Chu, "Epitaxial Growth of Hg-1212 Thin Films on SrTiO<sub>3</sub> Substrates", Physica C **277**, 219(1997).
5. J.Z. Wu, S.H. Yun, A. Gapud, B.W. Kang, W.N. Kang, S.C. Tidrow, D. Eckart, X.T. Cui and W.K. Chu, "Fast Temperature Ramping Hg-vapor Annealing Technique for Growth of Hg-Based Cuprate Thin Films", IEEE Trans. on Appl. Superconductivity, **7**, 1907(1997).
6. J.Z. Wu, S.H. Yun, W.N. Kang, B.W. Kang, A.A. Gapud, S.C. Tidrow, and D. Eckart, "Fabrication of High Quality Hg-1212 and Hg-1223 Thin Films", Proceedings of 10th Anniversary HTS Workshop on Physics, Materials and Applications, (World Scientific, Singapore), 89(1996).
7. J.Z. Wu and S.N. Tidrow, "Recent Progress in High-T<sub>c</sub> Superconducting Heterostructures", book chapter in *Thin Films: Heteroepitaxial Systems*, World Scientific, edited by W.K. Liu and M.B. Santos, Singapore (1999), P267.
8. S.H. Yun, J.Z. Wu, S.C. Tidrow, and D. Eckart, "Growth of Hg-1223 Thin Films on LaAlO<sub>3</sub> Substrate Using Fast Temperature Ramping Hg-vapor Annealing", Appl. Phys. Lett., **68**, 2656(1996).
9. U.S. patent #5843870 (1999), by J.Z. Wu and S.W. Yoo, "Alkaline-Doped Cuprate Superconductors", awarded May 1998.
10. U.S. patent pending, by J.Z. Wu, S.L. Yan, and Y.Y. Xie, "Thin Film Hg-Based Superconductors and Method of Fabrication Thereof", submitted April 1998.
11. T. Aytug, A.A. Gapud, S.W. Yoo, B.W. Kang and J.Z. Wu, "Effect of Na-doping on oxygen distribution of Hg-1223 superconductors", Physica C **312**, (1999).
12. A.A. Gapud et al, "Li-Doping-Assisted Growth of Hg-1223 Superconducting Phase in Bulks and Thin Films", Physica C **308**, 264(1998).
13. B.W. Kang, A.A. Gapud, X. Fei, T. Aytug, and J.Z. Wu, "Minimization of detrimental effect of air in Hg-1212 thin film processing", Appl. Phys. Lett. **72**, 1766(1998).
14. J.Z. Wu, S.W. Yoo, T. Aytug, A. Gapud, B.W. Kang, S. Wu, and W. Zhou, "Superconductivity in Sodium and Lithium Doped Mercury-Based Cuprates", Journal of Superconductivity **11**, 169 (1998).
15. J.Z. Wu, S.L. Yan, and Y.Y. Xie, "Cation Exchange: A New Scheme for Synthesis of High-Quality Epitaxial Hg-Based Superconducting Thin Films", Appl. Phys. Lett. **74**, 1469(1999).
16. L. Fang, S.L. Yan, A.A. Gapud et al, "Epitaxial Growth of Hg-1212 Very-Thin Films", submitted to Physica C.

17. S.L. Yan, Y.Y. Xie, J.Z. Wu, *et al*, "High Critical Current Density in Epitaxial Hg-1212 Thin Films", Appl. Phys. Lett. **73**, 2989(1998).
18. Y.Y. Xie, J.Z. Wu, A. Gapud, Y. Yu, and Y. Xin, "Synthesis of Hg-1223 superconductors using a cation-exchange process", submitted to Physica C.

### 3. Physical Properties of Hg-HTS Thin Films

#### 3.1. $J_c(T,H)$ —State-of-Arts and Ultimate Limits

Fig. 3 shows  $J_c$ s of several HTS thin films of the best quality. Data for Hg-1212 and Hg-1223 films were from our group. It is obvious that Hg-HTS films are superior to others at temperature above 77 K. At 100K,  $J_c \sim 2 \text{ MA/cm}^2$  can still be maintain in Hg-1212 films, which are orders of magnitudes higher than that obtained so far on any other superconductors. Almost all HTS films display a granular feature. The  $J_c$ , one of the most important parameters in evaluation of a superconductor, is thus determined by both intrinsic and extrinsic, factors on a superconducting film. The major extrinsic factor is the weak-links across the grain boundaries, which affects directly the temperature-dependence of  $J_c$ s. This is not hard to see from Fig. 3 via comparison of  $J_c$ s of Hg-1212 and Hg-1223 films. In fact, Hg-1223 has high  $T_c$  and thus is expected to have better  $J_c$ s at higher temperature. The opposite shown in Fig. 3, indicates, as we have confirmed from XRD pole figure study, that the poorer epitaxy on Hg-1223 films is responsible. This, on the other hand, suggests that by improving epitaxy of the Hg-1212 and Hg-1223 films, a better  $J_c(T)$  can be obtained.

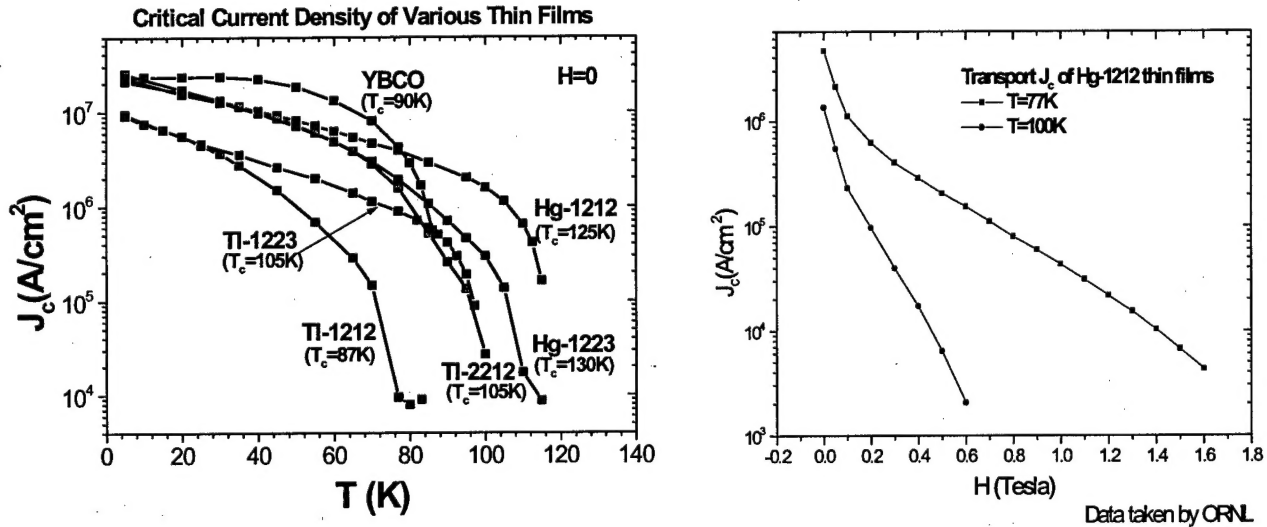


Fig. 3 Left panel: Temperature dependence of critical current densities of a few HTS films of the best quality. Right panel: field-dependence of critical current densities on Hg-1212 films at 77K and 100K

In an applied magnetic field above 1 Tesla,  $J_c$ s of Hg-HTS films fall below that of YBCO films. This is not unexpected since YBCO is (and the only one HTS which is) less anisotropic than Hg-HTSs do. Intrinsically,  $J_c$ s are determined by the irreversibility behavior, which in turn is associated to the anisotropy of the material. As lower anisotropy results in less decrease of  $J_c$ s

with increasing applied magnetic fields, reducing anisotropy becomes the key to a better field performance of the  $J_c$ . One effective way many groups have adopted is high-energy ion-beam irradiation. On Hg-HTS bulks, the IBM group has shown recently that the irreversibility line can be pushed up by more than 2 orders of magnitude in the field range of 0-10 Tesla [aa]. We have studied the effect of irradiation directly on Hg-HTS films and found that irreversibility line of the film can be pushed up by more than 20 K at a fixed field. This means that irreversible field of Hg-HTS films can be increased to 2-3 Tesla range, which is comparable to that of YBCO. Of course, the same effect may be realized via chemical substitution or doping in Hg-HTSs.

### 3.2. Pinning and Mixed-State Flux Dynamics

Magnetic flux dynamics in the superconducting mixed-state of Hg-HTSs has been a focus of this study because it relates directly to the applications of the Hg-HTS films. One subject we studied extensively is flux pinning strength, such as the scaling laws of the vortex activation energy, Hall effect, and vortex phase diagrams, of Hg-HTS films and modifications of these physical properties with ion-beam irradiation. The beams used include 1 MeV protons (producing point defects), 800 MeV protons (random oriented columnar defects), 5 GeV  $Xe^+$  (parallel columnar defects). Many interesting results have been obtained in this study including: (1) unusual scalings in vortex activation energy in Hg-1212 and Hg-1223 films; (2) significant enhancement in  $J_c$  (up to several orders of magnitude) by addition of various types of defects while columnar defects are much more efficient; (3) examination of Matthiessen's rule on Hg-1212 and Hg-1223 films with addition of point defects; and (4) observation of a nonlinear glassy vortex-liquid phase and resolving the controversial "pinning-dependence" of Hall conductivity.

### 2.3 Tl-1212 vs. Hg-1212-a Secret of High $T_c$ s

A comparative study of Hg-1212 and Tl-1212 ('1212' system) films in normal state and superconducting state revealed interesting similarity in the '1212' system. For example, the irreversibility fields of '1212' systems coincide over three decades when plotted as a function of reduced temperatures. This indicates that the main effect of replacement of Tl with Hg in the '1212' system is the changes caused charge carrier mobility, which was later revealed from a normal state Hall effect study and accounts for an over 30 K enhancement of  $T_c$ .

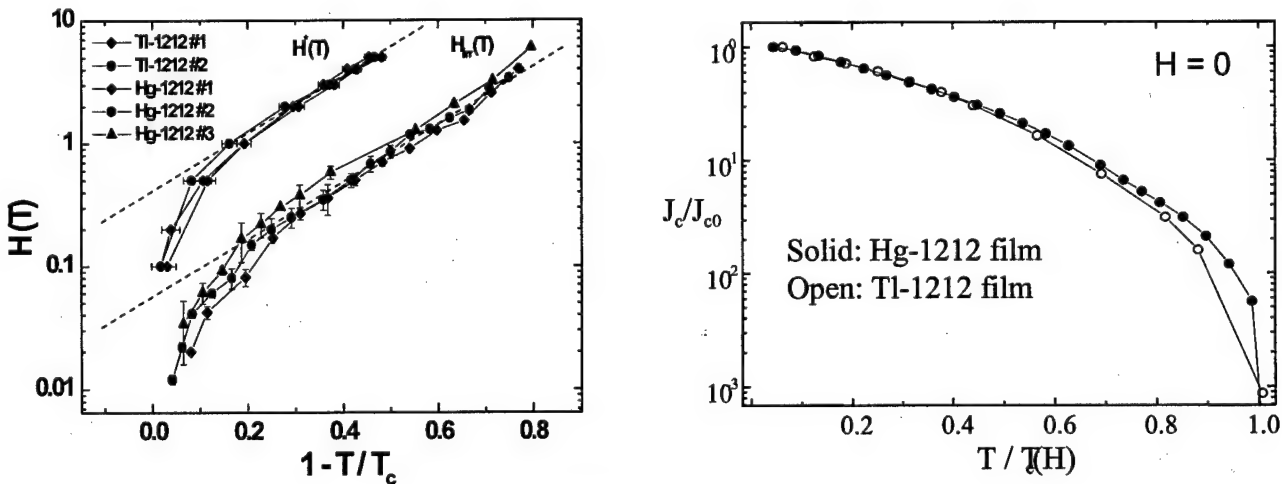


Fig. 3 Gopul et al.

Fig. 4 Left panel: coincidence of irreversibility lines of Hg-1212 and Tl-1212 films obtained in transport (the upper group curves) and magnetic (the lower group curves) measurements. Right panel: coincidence of  $J_c$ s of Tl-1212 and Hg-1212 films.

### Related Publications

1. U.S. patent pending, by W.K. Chu and J.Z. Wu, "Application of Cluster Ion Beam to Surface Smoothing of High Temperature Superconductors", transferred to EPION Co., March 1998.
2. B.W. Kang, J.Z. Wu, et al, "Pinning Dependence of the Hall Conductivity in the Glassy Vortex-Liquid Phase of High- $T_c$  Superconductors", submitted to Phys. Rev. Lett.
3. J.Z. Wu *et al*, "Enhancement of Pinning in Hg-1223 Thin Films using 5 GeV Xe ion Irradiation", submitted to Appl. Phys. Lett.
4. B.W. Kang, J.Z. Wu, A.A. Gapud, W.N. Kang, D.K. Christen and R. Kerchner, "Glassy vortex-liquid phase in high-  $T_c$  superconductors", submitted to Phys. Rev. Lett.
5. J.Z. Wu, B.W. Kang, W.N. Kang et al, "Sign Reversal in Mixed-state Hall Effect of Type-II Superconductors", submitted to Phys. Rev. B.
6. W.N. Kang, B.W. Kang, Q.Y. Chen, J.Z. Wu *et al*, "Scaling of the Hall Resistivity in Hg-1212 Thin Films with Columnar Defects", submitted to Phys. Rev. B.
7. A.A. Gapud, J.Z. Wu, B.W. Kang *et al*, "Critical Current Densities of Hg-1212 and Tl-1212 Thin Films", submitted to Appl. Phys. Lett.
8. A.A. Gapud, B.W. Kang, J.Z. Wu, S.L. Yan, Y.Y. Xie and M.P. Siegal, "Nature of giant  $T_c$  shift in '1212' superconductors due to Hg/Tl exchange", To appear in Phys. Rev. B.
9. B.W. kang, J.Z. Wu, W.N. Kang, Q.Y. Chen, W.K. Chu and Z.F. Ren, "Effect of anion doping on Hall sign anomaly", to appear in Philosophic Magazine Letters.
10. A.A. Gapud, J.R. Liu, J.Z. Wu, W.N. Kang, B.W. Kang, S.H. Yun and W.K. Chu, "Effects of 1-MeV Proton Irradiation on Hg-based Cuprate Thin Films", Phys. Rev. B. **56**, 862(1997).
11. J.R. Thompson, L. Krusin-Elbaum, D.K. Christen, J.L. Ullman, J.Z. Wu, Z.F. Ren, J.E. Tkaczyk, and J.A. Deluca, "Generic Enhancements of the Highest- $T_c$  Superconductors with GeV Protons", Appl. Phys. Lett. **71**, 536(1997).
12. B.W. Kang, J.Z. Wu, W.N. Kang, Q.Y. Chen, W.K. Chu, D.K. Christen, R.H. Kerchner, and A.A. Gapud, "Mixed-State Transport Properties of Hg-1212 Thin Films", Journal of Superconductivity **11**, 163 (1998).
13. W.K. Chu, Y.P. Li, J.R. Liu, J.Z. Wu, S.N. Tidrow, J. Matsuo and I. Yamada, "Smoothing of YBCO films by Cluster Beam Bombardment", Appl. Phys. Lett. **72**, 246(1998).
14. B.W. Kang, W.N. Kang, S.H. Yun, and J.Z. Wu, "Scaling Behavior of Pinning Potential in High Quality Hg-1212 Films", Phys. Rev. B **56**, 7862(1997).
15. A.A. Gapud, J.Z. Wu and S.L. Yan *et al*, "Magnetic Flux Pinning in Hg-based HTS Thin Films", Proc. of 8<sup>th</sup> US-JAPAN Workshop on High- $T_c$  Superconductors, Tellehasse, Florida, Dec. 8-10, 1997 (in press).
16. W.N. Kang, S.H. Yun, D.H. Kim, and J.Z. Wu, "Scaling Behavior and Mixed-State Hall Effect in Epitaxial Hg-1212 Thin Films", Phys. Rev. B **55**, 621(1997).

## 4. Device Applications of Hg-HTS Films

### 4.1. Microwave Characterization and applications passive devices

High-temperature superconductors (HTSs) are very attractive for microwave applications due to their low-loss performance in this frequency range. The high  $T_c$ s in Hg-HTSs and their relatively high irreversibility lines (compared to that of Tl-HTSs) make them appealing for microwave applications at temperatures above 100 K with compatible power handling capability. Considerable efforts had been put on characterization and optimization of microwave properties of Hg-HTS films and the results, which represent the best so far achieved on HTS thin films, are summarized in the following figures on both bare Hg-HTS films and prototypes passive devices such as micro-strip resonators and microwave shifters.

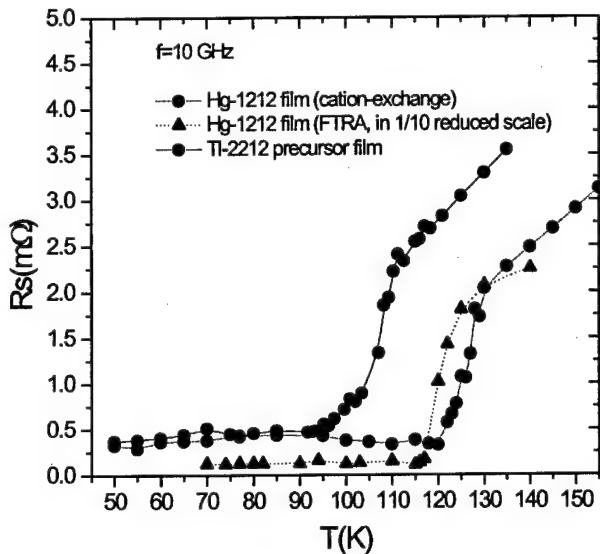
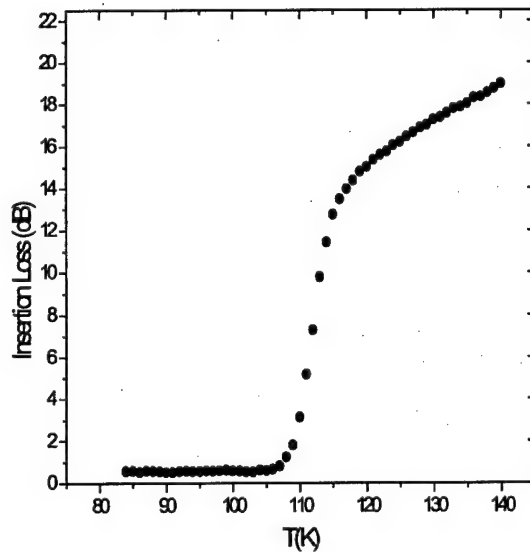
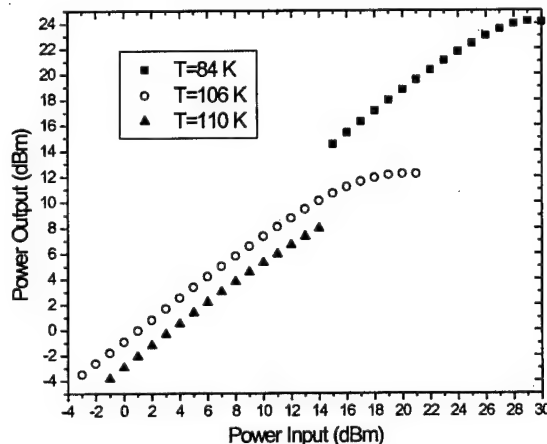


Figure 5. Surface Resistance of the three samples as a function of Temperature. Sample II curve must be multiplied by a factor of 10 to get the actual  $R_s$ .



Insertion Loss of a 5mm long 150 $\mu$ m wide microstrip line with copper ground plane.



Behaviour of power output from microstrip line as a function of input power at three different temperatures.



It is clearly shown that the low  $R_s$  and low loss, which are comparable with the best obtained on other HTSs (YBCO, Tl-HTSs) at  $\sim 77$  K can be maintained up to  $T_c \sim 120$  K on Hg-HTS films. Meanwhile, Hg-HTS films seem to have impressive power handling capability at temperatures near 110 K, as shown in the following figure. These results have demonstrated that Hg-HTS films are the best candidates for microwave devices that operate at temperatures above 100 K or higher.

#### 4.2. Grain-boundary Josephson Junctions (GBJJ)

Josephson junctions serve as the fundamental build block for a large class of superconducting electronics. To demonstrate the viability of Hg-HTSs for junction applications, we had worked planar-type JJs including GBJJs and e-beam irradiated JJs. Since the latter was hindered by problems in e-beam spot drifting, results reported here are mainly on GBJJs fabricated on bi-crystal  $\text{SrTiO}_3$  substrates with 24-degree grain boundaries. The I-V curves of Hg-HTS GBJJs resemble that of other HTS GBJJs at 77 K as expected. Such I-V behaviors degrade at 100K for Hg-HTS GBJJs and the reasons responsible for this degradation are still under investigation. One possibility is film degradation under standard photolithography process employed for fabrication of the Hg-HTS GBJJs. Film uniformity does not seem to be a factor as shown in the right panel of the following figure.

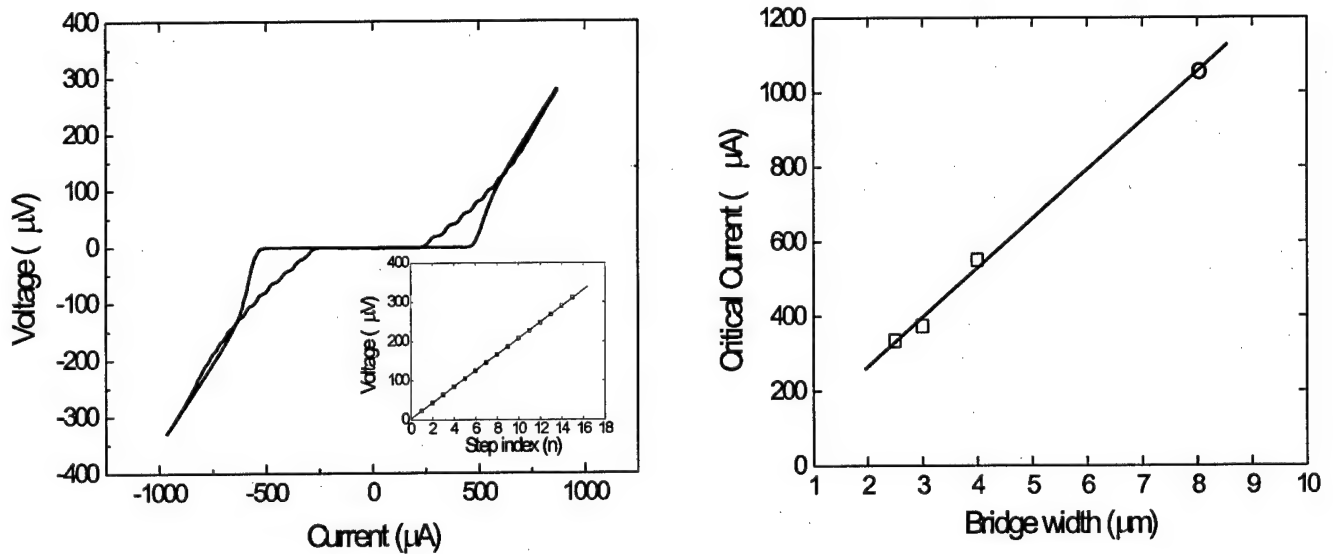
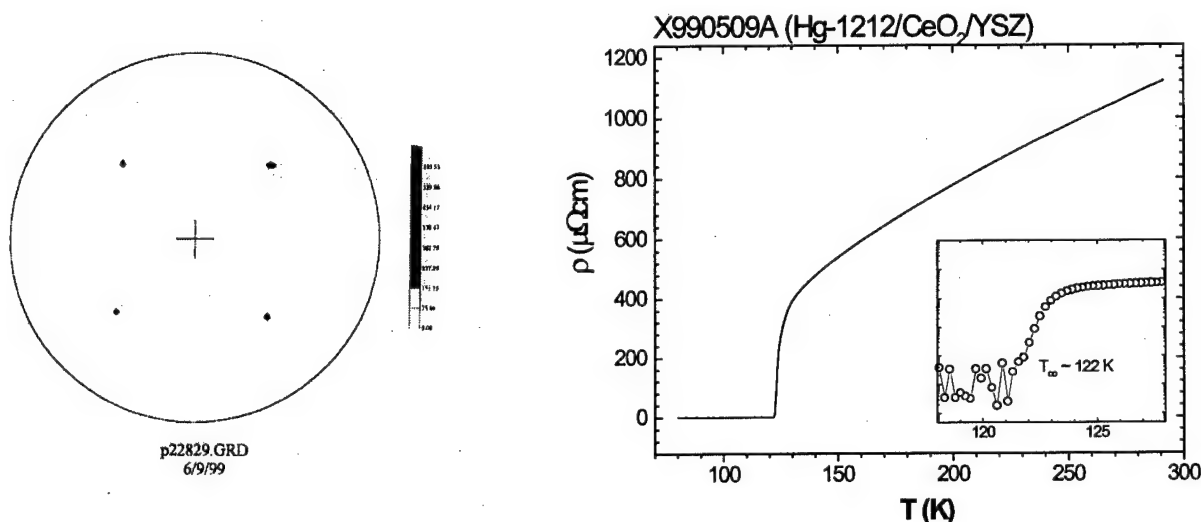


Fig 8. I-V curve of a Hg-1212 GBJ with 9.96 GHz microwave radiation at 77 K. The I-V curve without microwave radiation is presented for comparison. The inset is the voltage of Shapiro steps vs. the step index.

#### 4.3. Hg-HTS Coated Conductors

Hg-HTSs are one of the best candidates for power-related electrical applications due to the high  $T_c$ s and high  $J_c$ s demonstrated. In addition, the ex-situ process employed for fabrication of

Hg-HTS films may be advantageous in product scale-up in terms of lower cost and simpler processing. The major obstacle in Hg-HTS coated conductors is selection of appropriate buffers which can eliminate chemical inter-diffusion between Hg-HTSs and conducting substrates, and provide a template for epitaxy of Hg-HTS films. Our research on Hg-HTS coated conductors began a year ago, in collaboration with the Oak Ridge National lab and Los Alamos National lab. Several buffer architectures developed by ORNL and LANL have been used for growth of Hg-HTS films and preliminary results are promising. As shown in the following figure, epitaxial Hg-1212 films of  $\sim 1 \mu\text{m}$  thick have been achieved on Ni substrates with  $\text{CeO}_2/\text{YSZ}$  buffer layers. These films look smooth and have  $T_c$ s above 120 K. The transport critical current densities on these films are about one order of magnitude lower than that obtained on Hg-HTS films grown on  $\text{LaAlO}_3$  substrates. This is surprising as our experiments were still in the preliminary stage. The key point demonstrated in this study is the compatibility between Hg-HTSs and buffer architectures used for other HTSs on coated conductors. By optimizing the film processing



conditions and buffer layers, we should be able to increase  $J_c$  and other properties of the Hg-HTS coated conductors.

Fig 9. Left panel: XRD pole figure of Hg-1212 film grown on  $\text{CeO}_2/\text{YSZ}$  buffer Ni substrates. Right Panel: R-T curve of the same sample.

#### Related Publications

1. R.S. Aga, S.L. Yan, Y.Y. Xie, S.Y. Han, and J.Z. Wu, "Microwave surface resistance of Hg-1212 thin films", submitted to Appl. Phys. Lett.
2. Yang Yu, S.L. Yan, L. Fang, Y.Y. Xie, J.Z. Wu and Siyuan Han, H. Shimakage and Zhen Wang "Fabrication of  $\text{HgBa}_2\text{CaCu}_2\text{O}_y$  Grain Boundary Junctions Using the Cation Exchange Method", to appear in Supercond. Sci. & Tech. Vol. 12.
3. R.S. Aga, Y.Y. Xie, J.Z. Wu, et al, "Microwave power handling capability of Hg-1212 microstrip resonators", preprint.

4. Y.Y. Xie, T. Aytug, J.Z. Wu, D.K. Christen, et al, "Growth of Hg-1212 films on CeO<sub>2</sub>/YSZ buffered Ni tapes", preprint.
5. Y.Y. Xie, J.Z. Wu, A.A. Gapud et al, "Converting Tl-2212 microbridges to Hg-1212 microbridges using cation-exchange process", preprint.

## **5. Stability of Hg-HTS Thin Films**

The Hg-HTSs are very promising for various applications. It remains unclear, however, whether these films are stable in long term or in processes such as photolithography which are necessary for microelectronic applications. In particular, the severe air sensitivity of the cuprate precursors and the high volatile nature of Hg-compound make the issue of material stability in Hg-HTSs such an important research topic that no applications can be carried out without full knowledge of this issue. This motivated us to investigate the stability of Hg-based HTS films in routine operation environments (air, vacuum with thermal cycling), chemicals (alcohol, acetone, water) and standard photolithography process.

### **5.1. Environmental Stability**

Hg-HTS films are stable in vacuum and air. For example, in a test of thermal cycling between 77K to room temperature under low vacuum ( $\sim 1\text{mTorr}$ ), no sample degradation was observed on films after 14 consecutive cycles. In the test of film stability in air, two samples were measured every 6 months during a two-year period and the observed change in their superconducting properties is negligible. Sample degradation in air has been, however, observed on some films, few days or even hours after they were fabricated. This degradation becomes more severe when the sample is placed in humid air or water. Through careful experiments, it was discovered that the degradation is caused by un-reacted Ba-/Ca-containing compounds remained in the Hg-HTS films via the following route:



Such a mechanism is similar to that occurred to other HTSs (YBCO, Tl-HTSs, etc), especially in the early stage of material development due to existence of the impurity phases. This problem can be solved, or at least minimized by optimizing the processing conditions so that the precursors are fully reacted into superconductors with minimal traces of the impurity Ba-/Ca compounds.

### **5.2 Stability in Chemicals**

Hg-HTS films behave fairly stable in chemicals such as Acetone and Alcohol (see Fig. 10) This means many of existing sample processing techniques can be applied to Hg-HTS films without the needs of extra cautions.

### **5.3 Stability in Regular Photolithography Processes**

Several groups, including us, reported difficulties in patterning Hg-HTS films using the standard photolithography process. In order to pin point the reason, we break out the photolithography process into several steps and carried out a careful study of the sample

properties in each step using XRD, SEM, and transport/magnetic measurements. It is found that, after the heat treatment process of photoresist material, the superconducting properties of Hg-1212 samples are degraded as evidenced by a visible change in the surface terrace edges. However, there is no obvious surface contamination of the films observed after etching in an acid solution of HCl/H<sub>2</sub>O. It is suggested that lowering the baking temperatures (< 90 °C) during the heating process of photoresist may prevent the deterioration of the superconducting phases.

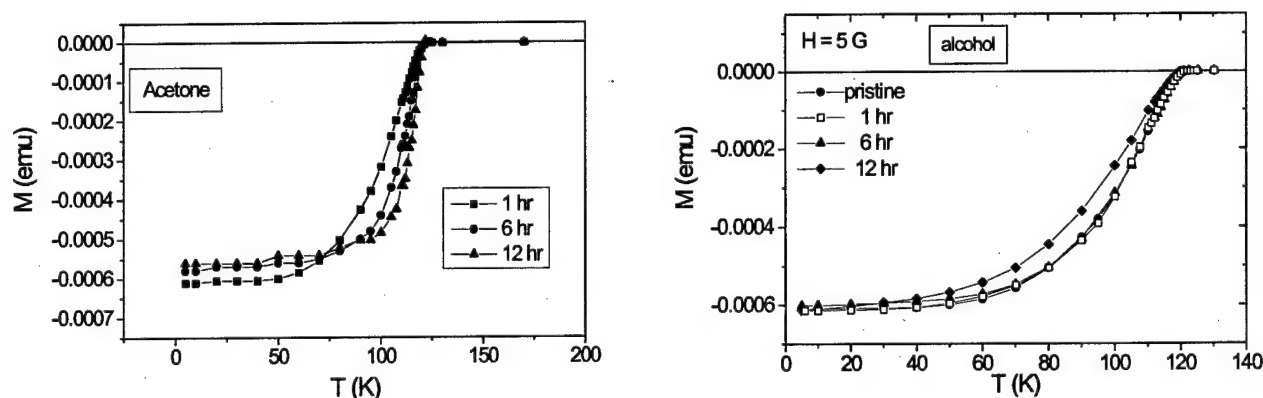


Fig. 10 Magnetization vs. temperature curves for Hg-HTS films soaked in Acetone (left) or Alcohol (right) for different periods.

## Related Publications

1. T. Aytug, B.W. Kang, S.L. Yan, Y.Y. Xie, and J.Z. Wu, "Stability of Hg-based Superconducting Thin Films", *Physica C* **307**, 117(1998).
2. T. Aytug, S.L. Yan, Y.Y. Xie, and J.Z. Wu, "Response of superconducting characteristics of Hg-1212 thin films to photolithographic processes", to appear in *Physica C*.

## PERSONNEL SUPPORTED

[List professional personnel supported by and/or associated with the research effort, by category below]

- Faculty: Judy Wu (one summer month each year for three years)
- Post-Docs: Dr. Xin Fei (five months, terminated in January 1998) and L. Fang (began from May 31, 1998 and terminated at Dec. 1, 1998).
- Graduate Students: B.W. Kang (12 months, Ph.D. 1998), Yiyuan Xie (24 months), Yu Yang (12 months), Robert Aga (18 months), and Tolga Aytug (three summer months).
- Other (please list role): none

## PUBLICATIONS

[List peer-reviewed publications submitted and/or accepted during the 36-month period starting from July 14 1996.]

## **SUBMITTED**

### **Books/Book Chapters**

#### **Journals**

1. Y.Y. Xie, J.Z. Wu, T. Aytug, A.A. Gapud, D.K. Christen, D.T. Verebelyi and K. Song, "Uniformity of the physical properties of large-area Hg-1212 thin films", submitted to Supercon. Sci. & Tech.
2. R.S. Aga, S.L. Yan, Y.Y. Xie, S.Y. Han, and J.Z. Wu, "Microwave surface resistance of Hg-1212 thin films", submitted to Appl. Phys. Lett.
3. W.N. Kang, B.W. Kang, Q.Y. Chen, J.Z. Wu, Y. Bai, W.K. Chu, D.K. Christen, R. Kurchner and S.I. Lee, "Triple Sign Reversal of Hall Effect in Hg-1212 Thin Films after Heavy-Ion Irradiation", submitted to Phys. Rev. Lett.
4. S.L. Yan, J.Z. Wu, L. Fang, Y.Y. Xie, T. Aytug, A.A. Gapud, and B.W. Kang, "Converting Tl-2212 thin films to Hg-1212 Thin films using cation-exchange process", submitted to J. Appl. Phys.
5. L. Fang, S.L. Yan, A.A. Gapud, T. Aytug, B.W. Kang, Y.Y. Xie, J.Z. Wu, S.C. Tidrow, M.H. Ervins, and K.W. Kirchner, "High-Temperature Superconductivity in very-thin Hg-1212 films", submitted to Appl. Phys. Lett.
6. J.Z. Wu, S.H. Yun, D. Christen *et al*, "Enhancement of Pinning in Hg-1223 Thin Films using 5 GeV Xe ion Irradiation", submitted to Appl. Phys. Lett.

## **PUBLISHED/ACCEPTED**

### **Books/Book Chapters**

7. J.Z. Wu and S.C. Tidrow, "Recent Progress in High- $T_c$  Superconducting Heterostructures", book chapter in *Thin Films: Heteroepitaxial Systems*, World Scientific, edited by W.K. Liu and M.B. Santos, Singapore (1999), P267.

#### **Journals**

8. Yang Yu, S.L. Yan, L. Fang, Y.Y. Xie, J.Z. Wu and Siyuan Han, H. Shimakage and Zhen Wang "Fabrication of  $\text{HgBa}_2\text{CaCu}_2\text{O}_y$  Grain Boundary Junctions Using the Cation Exchange Method", to appear in Supercond. Sci. & Tech. Vol. 12.
9. B.W. Kang, J.Z. Wu, *et al*, "Hall conductivity in high temperature superconductors", to appear in Phys. Lett. A.
10. Y.Y. Xie, J.Z. Wu, A. Gapud, Y. Yu, and Y. Xin, "Synthesis of Hg-1223 superconductors using a cation-exchange process", to appear in Physica C.
11. T. Aytug, S.L. Yan, Y.Y. Xie, and J.Z. Wu, "Response of superconducting characteristics of Hg-1212 thin films to photolithographic processes", to appear in Physica C.
12. Y.Y. Xie, J.Z. Wu, S.L. Yan, Y. Yu, T. Aytug and L. Fang, "Elimination of Air Detrimental Effect using Tl-assisted Growth process for Hg-1212 Thin Films", to appear in Physica C.
13. B.W. Kang, J.Z. Wu, A.A. Gapud, W.N. Kang, D.K. Christen and R. Kerchner, "Glassy vortex-liquid phase in high- $T_c$  superconductors", to appear in Phys. Rev. B.
14. L. Fang, S.L. Yan, A.A. Gapud *et al*, "Epitaxial Growth of Very-Thin Hg-1212 Films", IEEE Trans. Appl. Superconductivity 9, 2387 (1999).
15. A.A. Gapud, J.Z. Wu, B.W. Kang *et al*, "Critical Current Densities of Hg-1212 and Tl-1212 Thin Films", Appl. Phys. Lett. 9, 2387 (1999).
16. J.Z. Wu, S.L. Yan, and Y.Y. Xie, "Cation Exchange: A New Scheme for Synthesis of High-Quality Epitaxial Hg-Based Superconducting Thin Films", Appl. Phys. Lett. 74, 1469 (1999).



17. W.N. Kang, B.W. Kang, Q.Y. Chen, J.Z. Wu et al, "Scaling of the Hall Resistivity in Epitaxial Hg-1212 Thin Films with Columnar Defects", *Phys. Rev. B* **59** *Rapid Commun.* R9031 (1999).
18. A.A. Gapud, B.W. Kang, J.Z. Wu, S.L. Yan, Y.Y. Xie and M.P. Siegal, "Nature of giant  $T_c$  shift in '1212' superconductors due to Hg/Tl exchange", *Phys. Rev. B* **59**, 203(1999).
19. T. Aytug, A.A. Gapud, S.W. Yoo, B.W. Kang and J.Z. Wu, "Effect of Na-doping on oxygen distribution of Hg-1223 superconductors", *Physica C*, **312**, (1999).
20. B.W. Kang, J.Z. Wu, W.N. Kang, Q.Y. Chen, W.K. Chu and Z.F. Ren, "Effect of anion doping on Hall sign anomaly", *Philosophic Magazine Letters*, November 1998 issue.
21. S.L. Yan, Y.Y. Xie, J.Z. Wu, *et al*, "High Critical Current Density in Epitaxial Hg-1212 Thin Films", *Appl. Phys. Lett.* **73**, 2989(1998).
22. A.A. Gapud *et al*, "Li-Doping-Assisted Growth of Hg-1223 Superconducting Phase in Bulks and Thin Films", *Physica C* **308**, 264(1998).
23. T. Aytug, B.W. Kang, S.L. Yan, Y.Y. Xie, and J.Z. Wu, "Stability of Hg-based Superconducting Thin Films", *Physica C* **307**, 117(1998).
24. B.W. Kang, A.A. Gapud, X. Fei, T. Aytug, and J.Z. Wu, "Minimization of detrimental effect of air in Hg-1212 thin film processing", *Appl. Phys. Lett.* **72**, 1766(1998).
25. B.W. Kang, J.Z. Wu, W.N. Kang, Q.Y. Chen, W.K. Chu, D.K. Christen, R.H. Kerchner, and A.A. Gapud, "Mixed-State Transport Properties of Hg-1212 Thin Films", *Journal of Superconductivity* **11**, 163 (1998).
26. J.Z. Wu, S.W. Yoo, T. Aytug, A. Gapud, B.W. Kang, S. Wu, and W. Zhou, "Superconductivity in Sodium and Lithium Doped Mercury-Based Cuprates", *Journal of Superconductivity* **11**, 169 (1998).
27. W.K. Chu, Y.P. Li, J.R. Liu, J.Z. Wu, S.N. Tidrow, J. Matsuo and I. Yamada, "Smoothing of YBCO films by Cluster Beam Bombardment", *Appl. Phys. Lett.* **72**, 246(1998).
28. B.W. Kang, W.N. Kang, S.H. Yun, and J.Z. Wu, "Scaling Behavior of Pinning Potential in High Quality Hg-1212 Films", *Phys. Rev. B* **56**, 7862(1997).
29. J.R. Thompson, L. Krusin-Elbaum, D.K. Christen, J.L. Ullman, J.Z. Wu, Z.F. Ren, J.E. Tkaczyk, and J.A. Deluca, "Generic Enhancements of the Highest- $T_c$  Superconductors with GeV Protons", *Appl. Phys. Lett.* **71**, 536(1997).
30. A.A. Gapud, J.R. Liu, J.Z. Wu, W.N. Kang, B.W. Kang, S.H. Yun and W.K. Chu, "Effects of 1-MeV Proton Irradiation on Hg-based Cuprate Thin Films", *Phys. Rev. B.* **56**, 862(1997).
31. J.Z. Wu, S.H. Yun, A. Gapud, B.W. Kang, W.N. Kang, S.C. Tidrow, T.P. Monahan, X.T. Cui and W.K. Chu, "Epitaxial Growth of Hg-1212 Thin Films on  $\text{SrTiO}_3$  Substrates", *Physica C* **277**, 219(1997).
32. J.Z. Wu, *et al.*, "Fast Temperature Ramping Hg-vapor Annealing Technique for growth of Hg-based Cuprate Thin Films", *IEEE Trans. on Appl. Superconductivity* **7**, 1907(1997).
33. S.C. Tidrow, A. Tauber, W.D. Wilber, R.T. Lareau, C.D. Brandle, G.W. Berkstresser, A.J. Ven Graitis, and J.Z. Wu, "New Substrates For HTSC Microwave Devices", *IEEE Trans. on Appl. Superconductivity* **7**, 1766(1997).
34. W.N. Kang, S.H. Yun, D.H. Kim, and J.Z. Wu, "Scaling Behavior and Mixed-State Hall Effect in Epitaxial Hg-1212 Thin Films", *Phys. Rev. B* **55**, 621(1997).
35. J.Z. Wu, D. Eckart, S. H. Yun, and S. Tidrow, "Microstructures of Hg-Based Cuprate Thin Films", *Physica C* **271**, 1 (1996).

## Conferences

36. J.Z. Wu *et al.*, "Fabrication of High Quality Hg-1212 and Hg-1223 Thin Films", in *Proceedings of 10th Anniversary HTS Workshop on Physics, Materials and Applications*, (World Scientific, Singapore), 89 (1996).

37. A.A. Gapud, J.Z. Wu and S.L. Yan *et al*, "Magnetic Flux Pinning in Hg-based HTS Thin Films", Proc. of 8th US-JAPAN Workshop on High- $T_c$  Superconductors, Tallahassee, Florida, Dec. 7-10, 1997, P217.

## INTERACTIONS/TRANSITIONS

### ***Participation/Presentations At Meetings, Conferences, Seminars, Etc***

[Be selective, but be sure to include participation that reflect the quality/impact of the effort. Do not include conferences listed in "publications" above, unless you were keynote or panel speaker or were involved in some other significant capacity.]

### **Partial list of invited talks**

1. "Fabrication and Application of Hg-HTS Thin Films and Devices", the 9th US-Japan Workshop on High  $T_c$  Superconductivity, Yamanashi, Japan, Oct. 13-15, 1999.
2. "Growth of very-thin Hg-1212 films and their applications in IR sensors", US Army workshop on electronic, Photonic, Electro-Optical, and Electro-Magnetic Materials, Huntsville, Oct. 6-7, 1999.
3. "Hall Effect in HTSs", Workshop for new theories, discoveries, and applications of superconductors", Las Vegas, May 31-June 4, 1999.
4. "Mechanism of Hall sign reversals and vortex glassy-liquid phase", Argonne National lab, May 19, 1998.
5. "Transport Properties of Hg-HTS thin Films", Midwest Consortium of High- $T_c$  Superconductivity Annual Review Conference, Columbus, Ohio, Jan. 30, 1998.
6. "Pinning in Hg-based Superconducting Thin Films", the 8th US-Japan Workshop on High  $T_c$  Superconductivity, Tallahassee, FL Dec.8-10, 1997.
7. "Hall Effect of Hg-Based Superconductors", Workshop on "Flux, Quantum, and Mesoscopic Effects in Superconducting Materials and Devices", Santa Fe, August 4-8, 1997.
8. "Mixed-State Transport Properties of Mercury-Based Cuprate Thin Films", International Workshop on Tl- and Hg-Based Superconductors, Cambridge, England, May 25-28, 1997.
9. "Physical Properties of Hg-based Cuprate Thin Films", Material Research Society Annual Fall meeting, Boston, Nov. 28-Dec.2, 1996.
10. "Fabrication of Hg-Based Cuprate Thin Films", 10th Anniversary High  $T_c$  Superconductivity Workshop, Houston, March 12-16, 1996.
11. "Physical Properties of Hg-based Cuprate Thin Films", Interdisciplinary Center for Superconductivity, Univ. of Cambridge, Cambridge, UK, June 11, 1997.
12. "Mixed-State Transport Properties of Hg-based Superconductors", Department of Physics, Nanjing University, Nanjing, China, June 12, 1997.
13. "Hall Effect of Hg-based Superconductors", Center for Low Temperature Physics, University of Science and Technology of China, Hefei, China, June 17, 1997.
14. "Mixed-State Transport Properties of Hg-based Superconductors", Institute of Plasma Physics, Academic Sinica, Hefei, China, June 19, 1997.

### ***Consultative And Advisory Functions To Other Laboratories And Agencies***

[Consultative and advisory functions to other laboratories and agencies, especially Air Force and other DoD laboratories. Provide factual information about the subject matter, institutions, locations, dates, and name(s) of principal individuals involved.]

1. Scientific consultant for the Midwest Superconductivity Inc. at Lawrence, Kansas on the MOCVD HTS tape program. Contact: Dr. John Hack, R&D Director of MSI.
2. Scientific consultant for the US Army Research Lab at Maryland on the uncooled IR sensor material research program starting from July 1998.
3. Co-Chair of the Material Research task force for Senator Pat Roberts (US senator)'s advisory committee for Sciences, Technologies and Future of Kansas (since March 1999).

### ***Transitions***

[Describe cases where knowledge resulting from your effort is used, or will be used, in a technology application. Transitions can be to entities in the DOD, other federal agencies, or industry. Briefly list the enabling research, the laboratory or company, and an individual in that organization (\*\*with contact information, please\*\*) who made use of your research. Contact information is vital.]

## **NEW DISCOVERIES, INVENTIONS, OR PATENT DISCLOSURES**

1. U.S. patent 5843870 (1999), by J.Z. Wu and S.W. Yoo, "Alkaline-Doped Mercury Cuprate Superconductors".
2. U.S. patent 5883050 (1999), by S.H. Yun and J.Z. Wu, "Hg-Based Superconducting Cuprate Films and Methods and Apparatus for Preparing the Same".
3. U.S. and international patent pending, by J.Z. Wu, S.L. Yan, and Y.Y. Xie, "Thin Film Hg-Based Superconductors and Method of Fabrication Thereof", DKT No. 26273, April 1998.
4. U.S. patent pending, by W.K. Chu and J.Z. Wu, "Application of Cluster Ion Beam to Surface Smoothing of High Temperature Superconductors", transferred to EPION Co., March 1998.
5. Patent pending, by J.Z. Wu, "New thermoelectric materials and the methods for preparing the same", December 1998.

## **HONORS/AWARDS**

[List honors and awards (include dates) received during the grant/contract period. List lifetime achievement honors (include dates) such as Nobel prize, honorary doctorates, and society fellowships prior to this effort.]

- Dr. B.W. Kang, currently postdoctoral associate at the Oak Ridge National Lab, won a gold medal at MRS 1998 Annual Fall meeting Graduate student awards for her thesis work at the University of Kansas, supported by the AFOSR project.